

# PATENT ABSTRACTS OF JAPAN

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**(54) ELECTROCONDUCTIVE RESIN COMPOSITION, FUEL CELL SEPARATOR  
COMPRISING THE SAME, THE PRODUCTION THEREOF AND SOLID POLYMER TYPE  
FUEL CELL USING SAID FUEL CELL SEPARATOR**

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide an electroconductive resin composition that can be produced in large amounts and shows excellent high-temperature durability, high resistance to hydrolysis.

**SOLUTION:** This electroconductive resin composition is constituted with (A) 100 pts.wt. of a liquid crystal polyester resin forming an anisotropic molten phase, (B) 0.01-30 pts.wt. of a carbodiimide, (C) 50-3,000 pts.wt. of electroconductive carbonaceous powder, (D) 0-10,000 pts.wt. of a filler. This invention simultaneously provides a fuel cell separator made of the electroconductive resin composition, the production process therefor and a solid polymer type fuel cell using this fuel cell separator.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Field of the Invention] This invention relates to the polymer electrolyte fuel cell which uses the fuel cell separator which consists of a conductive resin composition and this conductive resin composition, its manufacturing method, and the fuel cell separator concerned.

**[0002]**

[Description of the Prior Art] A fuel cell is a device which transforms chemical energy into electrical energy directly by contacting the electrode of a couple via an electrolyte, supplying fuel to one side of this electrode, supplying an oxidizer to another side, and oxidizing fuel electrochemically within a cell.

Although there are some molds in this fuel cell with an electrolyte, the polymer electrolyte fuel cell which used solid polyelectrolyte membrane for the electrolyte attracts attention in recent years as a fuel cell with which high power is obtained.

[0003] Although this polymer electrolyte fuel cell takes out current from an external circuit by supplying the oxygen gas which is a fluid at an oxidant electrode about hydrogen gas which is a fluid to a fuel electrode, in each electrode, the reaction as shown in following (1) and (2) has produced it in this case.

**[0004]**

Fuel-electrode reaction:  $H_2 \rightarrow 2H^+ + 2e^-$  (1)

Oxidant-electrode reaction:  $2H^+ + 2e^- + 1/2O_2 \rightarrow H_2O$  (2)

[0005] Namely, hydrogen ( $H_2$ ) serves as a proton ( $H^+$ ) on a fuel electrode, A proton moves on an oxidant electrode in the inside of solid polyelectrolyte membrane, reacts to oxygen ( $O_2$ ) on

an oxidant electrode, and produces water ( $H_2O$ ), Therefore, supply of reactant gas, and discharge and extraction of current are needed for operation of a polymer electrolyte fuel cell, and further in a polymer electrolyte fuel cell. Usually, since operation under the wet atmosphere in the range of 120 \*\* or less will be assumed from a room temperature, therefore water will be treated by a liquid state, discharge of the water from supply management and the oxidant electrode of the water to a fuel electrode is needed.

[0006]On the other hand, a separator serves to make separate so that the fuel gas, oxidant gas, and cooling water which flow through the inside of a fuel cell may not be mixed among the parts which constitute a fuel cell.

It is a member as which gas barrier property, conductivity, corrosion resistance, etc. are required.

[0007]As a separator of the above-mentioned polymer electrolyte fuel cell, The advantageous thing is proposed in respect of productivity or cost, and these are the graphite composite materials which used various kinds of thermoplastics or thermosetting resin as the binder, For example, the separator with which thermoplastics like [ again / in JP,57-61752,A or JP,57-617521,A ] polypropylene and nylon was used for thermosetting resin as a binder is explained by JP,55-019938,A.

[0008]However, the separator by the graphite composite material which used these thermoplastics or thermosetting resin as the binder, Rather than the separator which machines and manufactures the graphite slab currently used from before, although excelled in the field of productivity or cost, there was a problem in high temperature durability and hydrolysis endurance in it.

[0009]

[Problem(s) to be Solved by the Invention]This invention solved the problem of the above conventional technologies, and it made providing the conductive resin composition excellent in high temperature durability and hydrolysis endurance as well as the ability to mass-produce as a main purpose.

[0010]

[Means for Solving the Problem]To achieve the above objects, composition of a conductive resin composition which this invention adopted, (A) Liquid crystal polyester resin which forms an anisotropic melt phase 100 weight sections, (B) carbodiimide compound 0.01 to 30 weight section, (C) conductivity carbonaceous powder 50 to 3000 weight section, (D) filler It consists of zero to 10000 weight section.

[0011]This invention provides simultaneously a polymer electrolyte fuel cell using a fuel cell separator which consists of the above-mentioned conductive resin composition, its manufacturing method, and said fuel cell separator.

[0012]Namely, a result examined per [ which whose specific resistance was / an artificer of this invention / low, and was excellent in a mechanical strength ] conductive resin composition, By using as a binder a resin composition which consists of liquid crystal polyester resin (LCP) and a carbodiimide compound to conductive carbonaceous powder, It finds out that the water resisting property of LCP which had become a problem in conventional technology was not only improved, but have low specific resistance as conductive composite, and also a mechanical strength and gas barrier property improve, and came to complete this invention.

[0013]

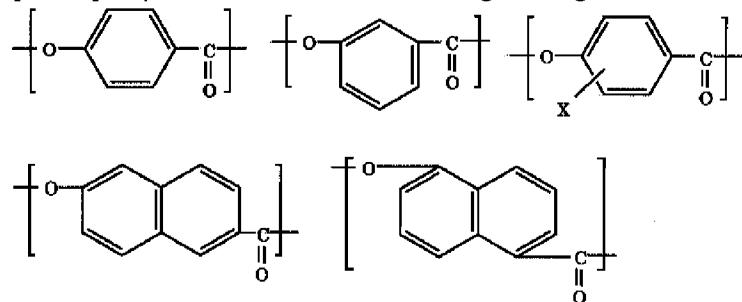
[Embodiment of the Invention]A detailed description of the invention is shown below.

[0014]The liquid crystal polyester used as a (A) ingredient by this invention is polyester called a thermotropic liquid crystal polymer, and can form an anisotropic melt phase. In this invention, the heat deflection temperature which is not changed as a constituent by the operating condition of a polymer electrolyte fuel cell uses not less than 80 \*\* of things [ 80 \*\* - 400 \*\* of ] (120 \*\* - 350 \*\*) still more preferably especially.

[0015]What the liquid crystal polyester used by this invention specifically becomes from the combination of (i) aromatic dicarboxylic acid and aromatic hydroxycarboxylic acid, (ii) The thing etc. which made aromatic hydroxycarboxylic acid react to polyester, such as what consists of aromatic hydroxycarboxylic acid of a different kind, a thing which consists of combination of (iii) aromatic dicarboxylic acid and aromaticdiol, and (iv) polyethylene terephthalate, are mentioned. Those ester plasticity derivatives may be used instead of these aromatic dicarboxylic acid, aromaticdiol, and aromatic hydroxycarboxylic acid.

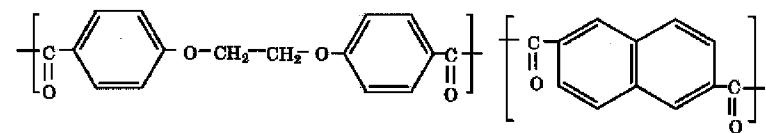
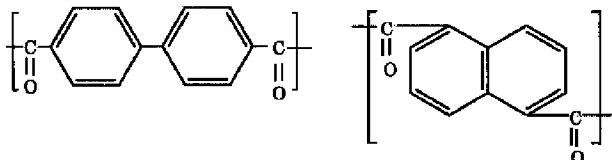
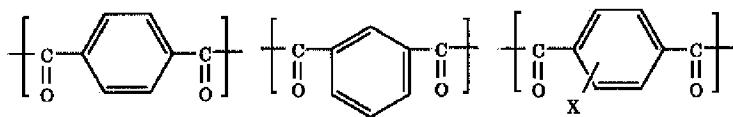
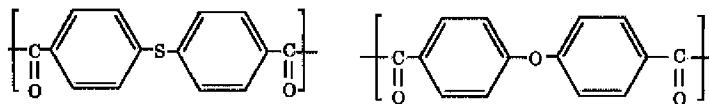
[0016]As a repeated structure unit of the above-mentioned liquid crystal polyester, although the following can be illustrated, it is not limited to these.

[0017]Repeated structure unit originating in aromatic hydroxycarboxylic acid : [Formula 1]

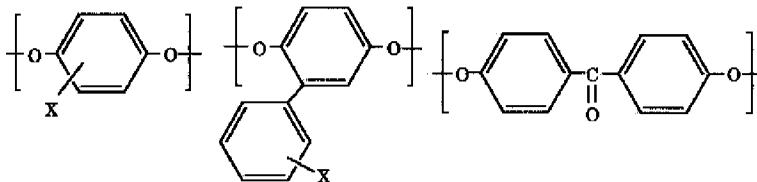
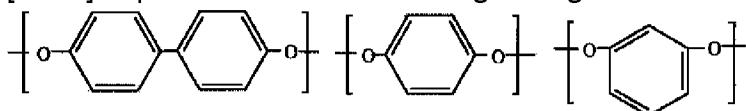


X in a formula expresses halogen, the allyl group, or the alkyl group (in the following structural formulae, it is the same.).

[0018]Repeated structure unit originating in aromatic dicarboxylic acid : [Formula 2]

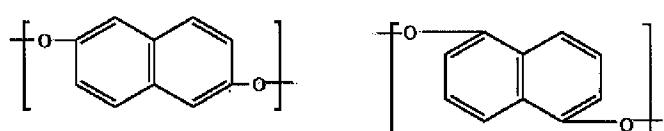
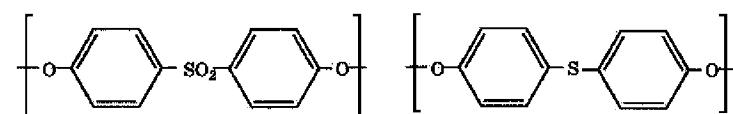
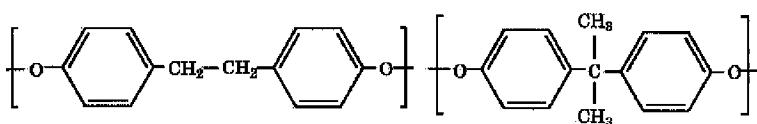
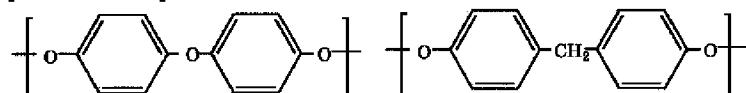


[0019]Repeated structure unit originating in aromaticdiol :[Formula 3]



[0020]

[Formula 4]



[0021]the repeated structure unit to which the above-mentioned liquid crystal polyester originates in aromatic hydroxycarboxylic acid from the balance of heat resistance, a mechanical property, and processability -- at least 30-mol % -- what is included is preferred.

[0022]As a carbodiimide compound used as a (B) ingredient by this invention, It is a compound which has one or more carbodiimide groups (-N=C=N-) in a molecule, It is mono- carbodiimide compound R-N=C=N-R or poly carbodiimide compound (-R-N=C=N-) n (R has one or more carbon atoms here, and n is two or more integers.) expressed with a lower type.

[0023]As the above-mentioned mono- carbodiimide compound, what was compounded by a method generally learned well can be used, For example, 3-methyl-1-phenyl-2-phospholene 1-oxide can be used for a carbodiimide-ized catalyst, and various isocyanates can be compounded by a decarboxylation condensation reaction in a non-solvent or an inert solvent at temperature of about 70 degrees or more.

[0024]As an example of a mono- carbodiimide compound, Dicyclohexylcarbodiimide, a diisopropylcarbodiimide, A dimethylcarbodiimide, a diisobutylcarbodiimide, a dioctylcarbodiimide, t-butylisopropylcarbodiimide, a diphenylcarbodiimide, A di-t-butylcarbodiimide, a di-beta-naphthyl carbodiimide, etc. can be mentioned and a JISHIKURO carbodiimide and a diisopropylcarbodiimide are industrially preferred from a point that acquisition is easy, especially in these.

[0025]A poly carbodiimide compound can also be manufactured by various methods, a manufacturing method (a U.S. Pat. No. 2941956 specification and JP,47-33279,B.) of a polycarbodiimide of the former fundamentally J. It can be based on Org.Chem, 28, 2069-2075 (1963), Chemical Review 1981, and Vol.81 No.4 p619-621. It can manufacture by specifically compounding an isocyanate end polycarbodiimide by a condensation reaction accompanied by carbon dioxide removal of organic diisocyanate.

[0026]In a described method, as organic diisocyanate which is the synthetic powder of a poly carbodiimide compound, For example, can use aromatic diisocyanate, aliphatic series diisocyanate, alicycle fellows diisocyanate, and these mixtures, and specifically, 1,5-naphthalene diisocyanate, 4, and 4'-diphenylmethane diisocyanate, 4,4'-diphenyldimethylmethane diisocyanate, 1, 3-phenylene diisocyanate, 1, 4-phenylene diisocyanate, 2, 4-tolylene diisocyanate, A mixture of 2, 6-tolylene diisocyanate, 2, and 4-tolylene diisocyanate and 2 and 6-tolylene diisocyanate, Hexamethylene di-isocyanate, the cyclohexane- 1, 4-diisocyanate, Xylylene diisocyanate, isophorone diisocyanate, the dicyclohexyl methane- 4, 4'-diisocyanate, Methylcyclohexane diisocyanate, tetramethyl xylylene diisocyanate, a 2,6-diisopropylphenyl isocyanate, the 1,3,5-triisopropyl benzene- 2, 4-diisocyanate, etc. can be illustrated.

[0027]In manufacture of a poly carbodiimide compound from the above-mentioned organic

diisocyanate, it can be controlled and used for a suitable degree of polymerization using a compound reacted to end isocyanates of a poly carbodiimide compound, such as a monoisocyanate.

[0028]Thus, as a monoisocyanate for closing an end of a polycarbodiimide and controlling to the degree of polymerization, For example, a phenylisocyanate, a tolyl isocyanate, a dimethylphenyl isocyanate, a cyclohexylisocyanate, a butylisocyanate, a naphthyl isocyanate, etc. can be illustrated.

[0029]To an active hydrogen compound which can react to an end isocyanate as encapsulant other than the above. Methanol which has - OH radical in aliphatic series, aromatic series, and an alicyclic compound, Ethanol, phenol, cyclohexanol, N-methylethanol amine, Diethylamine with a polyethylene-glycol monomethyl ether and polypropylene-glycol monomethyl ether;= NH group, Dicyclohexylamine; A butylamine with a -NH<sub>2</sub> group, Cyclohexylamine; a compound which has ethyl mercaptan, allyl mercaptan and a thiophenol with a succinic acid [ with - COOH group ], benzoic acid, and cyclohexane acid;-sulphydryl group, an epoxy group, etc. can be used.

[0030]A decarboxylation condensation reaction of the above-mentioned organic diisocyanate, Go on under existence of a carbodiimide-ized catalyst and as this catalyst, For example, 1-phenyl-2-phospholene 1-oxide, 3-methyl-1-phenyl-2-phospholene 1-oxide, Phospholene oxide, such as 1-ethyl-2-phospholene 1-oxide, 3-methyl-2-phospholene 1-oxide, and these 3-phospholene isomers, etc. can be used, A reactant field to 3-methyl-1-phenyl-2-phospholene 1-oxide is [ among these ] preferred.

[0031]By this invention, as a (C) ingredient as \*\*\*\* conductivity carbonaceous powder, Powder of scaly graphite, \*\*\*\*-like black lead, acetylene black, carbon black, Ketchen black, expanded graphite, and an artificial graphite can be mentioned, and the range of 5 micrometers - 80 micrometers of 10 nm - 100 micrometers can be preferably mentioned as the mean particle diameter.

[0032]As a filler used as a (D) ingredient by this invention, Organicity or an inorganic fiber can be used as a fibrous thing, and, specifically, glass fiber, milt glass fiber, an alumina fiber, silicon carbide fiber, ceramic fiber, an asbestos fiber, stone Coe textiles, a metal fiber, etc. can be illustrated.

[0033]As a filler, can also use granular organicity or an inorganic filler, and specifically, Huaras Tena Ito, a sericite, kaolin, mica, clay, bentonite, Silicate, such as asbestos, talc, and alumina silicate; Alumina, oxidized silicon, Metallic oxides, such as magnesium oxide, zirconium oxide, and titanium oxide; Calcium carbonate, Sulfate, such as carbonate; calcium sulfate, such as magnesium carbonate and dolomite, and barium sulfate; a glass bead, boron nitride, silicon carbide, Salo Jan, silica, etc. can be illustrated, and these may be hollow or porosity.

[0034]These reinforcing members may be beforehand processed by processing agents

generally used as a finishing agent, such as silane coupling material, a carbodiimide, and various emulsions, in order to raise adhesion with above-mentioned LCP which is a binder. [0035]It \*\*, and although a conductive resin composition of this invention consists of each ingredient of (A) thru/or (D) which explained [ above-mentioned ], it is as follows about a quantitative ratio in them.

(A) Liquid crystal polyester resin which forms an anisotropic melt phase 100 weight sections, (B) carbodiimide compound 0.01 to 30 weight section -- desirable -- the 0.5 - 5 weight-section (C) conductivity carbonaceous powder 50 - 3000 weight sections -- desirable -- 100 - 2000 weight section and (D) filler Zero to 10000 weight section [0036]If 0.01 or more weight sections of (B) ingredients are especially 0.5 or more weight sections, hydrolysis endurance and gas barrier property will improve, and if it is especially five or less weight sections, 30 or less weight sections of low electrical resistance required for a separator can be maintained.

[0037]If the (C) ingredient is 50 or more weight sections, electrical resistance can be made low, and if it is 3000 or less weight sections, a mechanical strength required for a separator can be maintained. If it is the range of 100 to 2000 weight section, these effects can be heightened further.

[0038](D) Also about an ingredient, if it is 10000 or less weight sections, a mechanical strength required for a separator can be maintained.

[0039]On the other hand, a fuel cell separator of this invention can be manufactured by fabricating a conductive resin composition which mixed above-mentioned (A) - (D) ingredient in separator shape in accordance with a manufacturing method of this invention.

[0040]That is, although above-mentioned (A) - (D) ingredient is first mixed so that it may become within the limits of the above-mentioned quantitative ratio, and a conductive resin composition is manufactured, as the manufacturing method, it is preferred to carry out melt kneading of the (A) - (D) ingredient. For example, if melt kneading is carried out at temperature of 200 \*\* - 400 \*\* using the Bambari mixer, a rubber roll machine, a kneader, a monopodium, or a twin screw extruder, it can be considered as a conductive resin composition.

[0041]Before performing this melt kneading method, in order to raise further the dispersibility of liquid crystal polyester resin and conductive carbonaceous powder, a mixing process by conventionally publicly known mixing methods, such as a \*\*\*\* stick, a ball mill, a sample mixer, a static mixer, and a ribbon blender, may be put in.

[0042]In this way, although an obtained conductive resin composition may be applied to a process fabricated in separator shape with a molten state, If needed, it may be good also as a pellet and this pellet may once be further dried by conventionally publicly known methods, such as fluidized bed drying, warm air circulation desiccation, vacuum drying, and vacuum fluidized bed drying.

[0043]Finally, fabricate this conductive resin composition in arbitrary polymer electrolyte fuel

cell circumference separator shape, and this shaping, Injection molding, compression molding, ejection-compression molding, transfer molding, extrusion molding, It can perform by combining a forming process of one kind of \*\*\*\*\*, or two or more kinds of forming processes from conventionally publicly known forming processes, such as hydrostatic molding, a belting press, press forming, and roll forming, and injection molding is advantageous to mass production especially.

[0044]As shape of a separator, have a role which covers a fuel electrode and an oxidizing agent pole, and. A plate-like thing which has a gas passageway which lengthened an overall length and was bent to a complicated pattern, and at least one breakthrough called a manifold, respectively is common so that fuel and oxidant gas can be efficiently diffused in a fuel cell. What is not provided with either one of a gas passageway or a manifold exists in a separator.

[0045]In this way, although a fuel cell of this invention is assembled and generating operation is carried out using an obtained polymer electrolyte fuel cell separator, as the assembly method and an operating method, the following can be mentioned, for example.

[0046]Namely, a fuel cell cell which sticks a fuel electrode and an oxidant electrode to two fields of an electrolyte layer which consists of solid polyelectrolyte membrane, respectively, and is allotted, A separator of this invention which has two or more channels for fuel gas and manifolds which were allotted to the side by the side of a fuel electrode of a fuel cell cell, A cell made to come to stick a separator of this invention which has two or more channels for oxidant gas and manifolds which were allotted to the side by the side of an oxidant electrode of a fuel cell cell to the fuel electrode and oxidant electrode side, respectively is assembled. And generating operation is performed, as make an electric insulating plate for electric insulation placed between those both ends, laminate two or more these cells to series, allocate a clamping plate and application-of-pressure maintenance is carried out, fuel gas is supplied to a fuel electrode, oxidant gas is supplied to an oxidant electrode again and a direct current is acquired.

[0047]

[Example]Hereafter, although the example of this invention is shown, this invention is not limited to this.

[0048]Examples 1 thru/or 3 and 590 g of comparative example 1,24,4'-dicyclohexylmethane diisocyanate, 62.6g of cyclohexylisocyanates, and 6.12 g of carbodiimide-ized catalysts (3-methyl-1-phenyl-2-phospholene 1-oxide). It was made to react at 180 \*\* for 48 hours, and poly (4,4'-dicyclohexyl methane) carbo JIMIDO (average degree of polymerization = 100 or less) was obtained.

[0049]By the presentation shown in following Table 1, LCP{all aromatic system thermoplastic polyester, The heat deflection temperature (18.6kg/[mm]<sup>2</sup>) of 240 \*\* (in the following and an example, it is the same.)}, (4,4'-dicyclohexyl methane) Melt kneading of a polycarbodiimide (all

over Table 1, abbreviated is carried out to PCD), conductive carbonaceous powder (all over Table 1, abbreviated is carried out to C), and the filler (all over Table 1, abbreviated is carried out to FR) was carried out with the twin screw extruder, and the masterbatch was created. From this masterbatch, the injection molding machine was used, the multiple-purpose dumbbell (10 mm in width, 4 mm in thickness, and 100 mm in length) specified to JIS K713 was created, and it was considered as the specimen. Number of copies in Table 1 shows the weight section.

[0050]Physical properties were measured by the following methods about each specimen. (Bending test) The universal testing machine 5544 type made from Instron was used, and flexural strength was measured by a part for bearing-distance [ of 50 mm ], and test period/of 0.5 mm.

(Specific resistance) The product sigma-10 type made from Nakamura SEIMITSU was used, and it measured by 4 terminal method.

[0051]

[Table 1]

	L C P 重量部	PCD 重量部	C 重量部	F R 重量部	固有抵抗 (mΩ・cm)	曲げ強度 (kgf/cm <sup>2</sup> )
実施例 1	100	2	100		18.7	4.68
実施例 2	100	2	900		4.3	4.52
実施例 3	100	2	900	100	4.0	6.96
比較例 1	100		400		18.9	4.23
比較例 2	100		900		5.5	4.35

[0052]The bending test after carrying out 200 time processings in 120 \*\* hot water, and measurement of specific resistance were performed using the specimen created in example 4 Example 1. A result is shown in the following table 2.

[0053]The specimen created by the comparative example 3 comparative example 1 was used, and the same operation as Example 4 was performed. A result is shown in the following table 2.

[0054]

[Table 2]

	曲げ強度 (kgf/cm <sup>2</sup> )	固有抵抗 (mΩ・cm)
実施例 4	4.68	18.7
比較例 3	2.50	40.5

[0055]Melt kneading of Example 5 - 7LCP, a poly(4,4'-dicyclohexyl methane) carbodiimide, conductive carbonaceous powder, and the filler was carried out with the twin screw extruder by the presentation of Examples 1-3, and the masterbatch was created. From this masterbatch, the injection molding machine was used, the fuel cell separator with a size 100 mm-square x thickness of 2 mm was fabricated, and the moldability of this fuel cell separator and density were measured.

[0056]The polymer electrolyte fuel cell was assembled using the separator for these fuel cells, the power generation examination was done for 200 hours, and the voltage drop rate over initial voltage was computed by having measured voltage. The various physical properties of a separator and the performance of a fuel cell are what was excellent as shown in the following table 3, and are \*\*\*\*\*.

[0057]Melt kneading of the comparative example 4 - 5LCP, and the conductive carbonaceous powder was carried out with the twin screw extruder by the presentation of the comparative examples 1 and 2, and the masterbatch was created. From this masterbatch, the injection molding machine was used, the fuel cell separator with a size 100 mm-square x thickness of 2 mm was fabricated, and the moldability of this fuel cell separator and density were measured.

[0058]The polymer electrolyte fuel cell was assembled using the separator for these fuel cells, the power generation examination was done for 200 hours, and the voltage drop rate over initial voltage was computed by having measured voltage. The various physical properties of a separator and the performance of a fuel cell are what was inferior as shown in the following table 3, and are \*\*\*\*\*.

[0059]

[Table 3]

樹脂組成物の組成		実施例5	実施例6	実施例7	比較例4	比較例5
セパレータ	密度(g/cm <sup>3</sup> )	1.84	1.80	1.80	1.60	1.65
	ガス透過率 (ml/m <sup>2</sup> ・day・atm)	6	15	17	1000	2000
燃料電池	200時間後の 電圧降下率	100%	99%	99%	60%	50%
セパレータの成形性(外観)	良好	良好	良好	不良	不良	

[0060]

[Effect of the Invention]The fuel cell separator using the conductive resin composition of this invention so that clearly from the above example and comparative example, Since the carbodiimide compound is contained, high humidity endurance and hydrolysis endurance outstanding also on the operating condition of a fuel cell called the bottom of 120 \*\* wet atmosphere from the room temperature can be demonstrated, and the operation stability of a fuel cell and endurance can be raised.

[0061]Since the conductive resin rough product of this invention is using liquid crystal polyester resin as main resinous principles, Since injection molding can be adopted as a production process of a fuel cell separator and easy mass production is attained, the production cost of a fuel cell separator can be lowered and productivity can be raised more.

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[Translation done.]